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TITAN: AEROSOL PHOTOCHEMISTRY AND VARIATIONS RELATED TO THE SUNSPOT CYCLE[1]

MARK ALLEN
Division of Geological and Planetary Sciences, California Institute of Technology

JOSEPH P. PINTO
Goddard Institute for Space Studies

AND

YUK L. YUNG
Division of Geological and Planetary Sciences, California Institute of Technology
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ABSTRACT

A photochemical theory is proposed for producing complex polymers in a methane atmosphere. It is argued that the polyacetylenes ($C_{2n}H_2$) are the most likely precursor molecules for the formation of the stratospheric haze layer on Titan. The production of polyacetylenes involves a strong positive feedback, leading to more production of polyactylenes. The thermosphere of Titan may undergo substantial expansion and contraction over a solar cycle, with important consequences for the chemistry of the upper atmosphere.

Subject headings: planets: atmospheres — planets: satellites — planets: Saturn — Sun: activity

I. INTRODUCTION

Recent observations by Lockwood (1977) and Lockwood and Thompson (1979) show that the geometric albedo of Titan in the visible has varied by about 10% in the last decade. A critical analysis of the data was presented by Suess and Lockwood (1980). The authors demonstrated the possible existence of a correlation between the secular brightness variations and the 11 yr sunspot cycle and further suggested that a photochemical smog might be responsible for these variations.

The existence of an absorbing haze, Danielson dust (Axel 1972), in the upper atmosphere of Titan was first proposed by Danielson, Caldwell, and Larach (1973). The best direct observations of the Danielson dust were reported recently by Tomasko (1979). A photochemical origin for the Danielson dust has been suspected and studied for many years (Strobel 1974; Caldwell 1977; Hunten 1977; Scattergood and Owen 1977; Bar-Nun and Podolak 1979; Chang *et al.* 1979). However, no specific photochemical scheme has been proposed.

In this *Letter*, we present the preliminary results of a new theory for the synthesis of long-chain carbon molecules. The theory is based on recent advances in our understanding of the photochemistry of acetylene (Laufer and Bass 1979), the chemistry of the interstellar medium (Mitchell and Huntress 1979), and the chemistry of soot formation (Homann, Warnatz, and Wellmann 1976). In addition, we discuss a mechanism by which the atmosphere of Titan can amplify its response to variations in the solar ultraviolet flux. Indeed, Titan may be a particularly useful object in the solar system for observing and documenting the effects of the sunspot cycle on planetary atmospheres.

II. PHOTOCHEMICAL MODEL

The primary driving force for photochemistry in the atmosphere of Titan is photodissociation of methane by sunlight shortward of 1600 Å. The globally averaged photon flux is 8.3×10^8 cm^{-2} s^{-1} at Lα and 9.9×10^8 cm^{-2} s^{-1} in the continuum for medium solar activity (Ackerman 1971). Hence, the maximum column integrated photolysis rate S is 1.8×10^9 cm^{-2} s^{-1}. However, the atmosphere of Titan extends considerably above the "surface" (Hunten 1977), defined in our model as the level $r = r_0 = 2900$ km from the center of the satellite. For a 160 K isothermal atmosphere of the type investigated by Danielson, Caldwell, and Larach (1973) and Strobel (1974) and adopted in this study, absorption of solar Lα occurs as far as $r = 2.4r_0$ on a tangential path, while absorption in the long-wavelength continuum takes place at $r \lesssim 1.2r_0$. The overall enhancement factor in S is about 3 in this case. The response of the thermosphere to the solar cycle can be dramatic and can lead to even larger values of S. A doubling of the EUV flux at solar maximum (Heath and Thekaekara 1977; Mount, Rottman, and Timothy 1980) could easily heat up the thermosphere by as much as 40 K, based on simple thermal-modeling arguments (Strobel and Smith 1973). An isothermal thermosphere at 200 K would absorb all incident Lα photons as far as $r = 3.6r_0$, enhancing the value of S by a factor of 8. The actual enhancement is probably less than this because of the destruction of CH_4 in the thermosphere and resonant scattering of Lα by atomic hydrogen. The effect will also be less if the bulk atmosphere of Titan is composed of inert gases such as N_2, Ne, or Ar. Thus,

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over a solar cycle, there could be as much as a factor of 5 variation in the direct photolysis rate of methane. In our steady state model, the quiescent, average, and active stages of the solar cycle are simulated by choosing $S = 5 \times 10^9$, 1×10^{10}, and 2×10^{10} cm^{-2} s^{-1}, respectively.

The set of photochemical reactions appropriate for the atmosphere of Titan is adopted from Strobel (1973, 1974) with updates by Yung and Strobel (1980). However, the chemistry of the polyacetylenes is new and is summarized in Figure 1 and Table 1, along with preferred values for the rate coefficients. Laufer and Bass (1979) argue that the major pathway for photolysis of C_2H_2 is (see R2, Table 1):

$$C_2H_2 + h\nu \rightarrow C_2H + H.$$

The quantum yield of this reaction was estimated by Payne and Stief (1976) to be 0.1 at Lα for pressures >50 millibars and measured by H. Okabe (1980, private communication) to be 0.6–0.7 at 1470 Å for pressures <1 torr. We adopt a quantum yield of 0.6 for all wavelengths in our calculations. The ethynyl radical produced in reaction R2 can readily attack another C_2H_2 to form butadiyne (Laufer and Bass 1979) (see R3, Table 1):

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H.$$

Based on the studies by Cullis, Hucknall, and Shepherd (1973), Homann, Warnatz, and Wellmann (1976), and Tanzawa and Gardiner (1980), we propose that the higher polyacetylenes can be formed by displacement reactions such as R23, R24, and R25 in the atmosphere of Titan. In our model, we do not go beyond C_8H_2, and we assume that polyacetylenes heavier than C_8H_2 are irreversibly removed from the system in the form of Danielson dust. The production rate of dust is not sensitive to where the chain is terminated. The optical properties of this polymeric dust should be similar to soot, whose index of refraction in the visible is 1.56–0.46i (Park and Appleton 1973). Moreover, compounds with a sequence of conjugated multiple bonds are colored (Roberts and Caserio 1964). Thus polyacetylenes of appropriate length can have enhanced absorption in the blue and may account for the reddish colors at the poles of Titan, where Danielson dust is more abundant (Tomasko 1979).

III. RESULTS AND DISCUSSION

The model atmosphere we adopt is composed primarily of methane at a constant temperature of 160 K. The bottom level corresponds to $r = r_0 = 2900$ km, where the number density and pressure are 1×10^{17} cm^{-3} and 2.4 millibars, respectively. The equations of continuity are solved for 17 species: H, H_2, CH, $^1CH_2$, $^3CH_2$, CH_3, C_2H, C_2H_3, C_2H_5, C_4H, C_6H, C_2H_2, C_2H_4, C_2H_6, C_4H_2, C_6H_2, and C_8H_2. Vertical transport, as parametrized by molecular and eddy diffusion, is allowed for all species. A zero flux is specified as the upper boundary condition for all the hydrocarbons. At the lower boundary, the short-lived hydrocarbons have zero flux, while the long-lived ones (C_2H_6 and C_2H_2) can leave the system with maximum eddy velocity. Atomic and molecular hydrogen can escape at their respective effusion velocities at the upper boundary, but the fluxes at the lower boundary are zero. The eddy diffusivity profile is assumed to have the same functional form as the one used by Yung and Strobel (1980) with $\gamma = \frac{1}{2}$. At the lower and upper boundary, the values for the eddy diffusion coefficient are 1×10^5 and 1×10^7 cm^2 s^{-1}, respectively. In the standard model, we chose $S = 1 \times 10^{10}$ cm^{-2} s^{-1} for the photolysis of CH_4.

The number densities for the major hydrocarbon species are shown in Figure 2. H_2 is an abundant photochemical product, whose mixing ratio is about 3%. This model is consistent with the observational constraints for C_2H_6, C_2H_4, C_2H_2, and H_2 (Gillett 1975; Münch, Trauger, and Roesler 1977), given the uncertainties of these observations (Caldwell 1977). The column integrated dust production rate is 2.2×10^{-13} g cm^{-2} s^{-1} and should supply sufficient material for the formation of aerosol particles (Pollack *et al.* 1980). The escape fluxes of H and H_2 are, respectively, 3.6 and 3.4×10^{10}

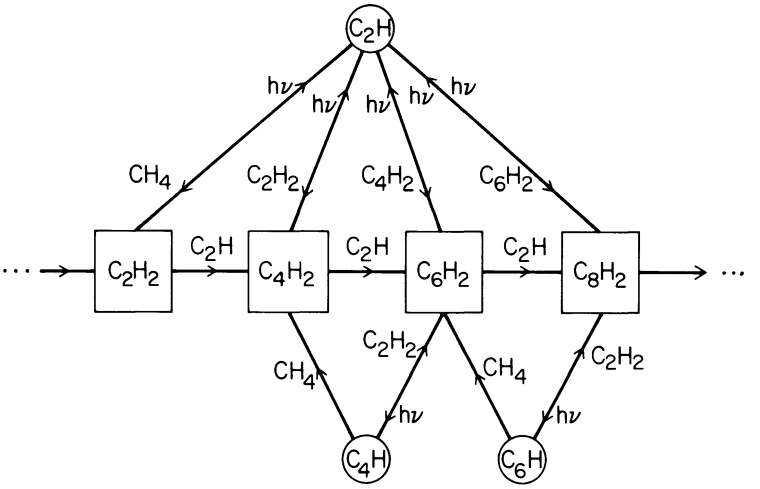

FIG. 1.—Schematic diagram showing the formation, recycling, and loss of polyacetylenes in the atmosphere of Titan

cm^{-2} s^{-1} and could provide a large source of hydrogen to the torus. After being ionized, these toroidal particles may form a low-energy plasma, whose density is estimated to be as high as 100 cm^{-3}. From the observations of Judge, Wu, and Carlson (1980), we estimate the lifetime for atomic hydrogen to be on the order of a few days and the flux of hydrogen escaping from Titan to be $\sim 1 \times 10^{10}$ atoms cm^{-2} s^{-1}. These values are consistent with our current model. It should be noted that the major dissociation path for CH_4 in our model is the

TABLE 1

PARTIAL LIST OF REACTIONS AND RATE COEFFICIENTS USED IN STANDARD PHOTOCHEMICAL MODEL[a]

Number	Reaction	Rate Coefficient	Reference
R1.....	$CH_3 + h\nu \rightarrow {}^3CH_2 + H$	$J_1 = 5.4(-7)$	1, 2, 3
R2.....	$C_2H_2 + h\nu \rightarrow C_2H + H$	$J_2 = 3.7(-8)$	4, 5, see text
R3.....	$C_4H_2 + h\nu \rightarrow 2C_2H$	$J_3 = 8.0(-7)$	6, 7
R4.....	$C_6H_2 + h\nu \rightarrow C_4H + C_2H$	$J_4 = J_3$	8
R5.....	$C_8H_2 + h\nu \rightarrow C_6H + C_2H$	$J_5 = J_3$	8
R6.....	${}^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + 2H$	$k_6 = 5.3(-11)$	9
R7.....	${}^3CH_2 + CH_3 \rightarrow C_2H_4 + H$	$k_7 = 5.0(-11)$	10
R8.....	$C_2H + C_2H_2 \rightarrow C_4H_2 + H$	$k_8 = 1.0(-10)\ \exp(-361/T)$	5
R9.....	$C_4H + C_2H_2 \rightarrow C_6H_2 + H$	$k_9 = k_8$	8
R10.....	$C_6H + C_2H_2 \rightarrow C_8H_2 + H$	$k_{10} = k_8$	8
R11.....	$C_2H + CH_4 \rightarrow C_2H_2 + CH_3$	$k_{11} = 3.0(-11)\ \exp(-1400/T)$	5, 8
R12.....	$C_4H + CH_4 \rightarrow C_4H_2 + CH_3$	$k_{12} = k_{11}$	5, 8
R13.....	$C_6H + CH_4 \rightarrow C_6H_2 + CH_3$	$k_{13} = k_{11}$	5, 8
R14.....	$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5$	$k_{14} = 3.0(-11)\ \exp(-1200/T)$	5, 8
R15.....	$C_4H + C_2H_6 \rightarrow C_4H_2 + C_2H_5$	$k_{15} = k_{14}$	5, 8
R16.....	$C_6H + C_2H_6 \rightarrow C_6H_2 + C_2H_5$	$k_{16} = k_{14}$	5, 8
R17.....	$C_2H + H_2 \rightarrow C_2H_2 + H$	$k_{17} = 3.0(-11)\ \exp(-1600/T)$	5, 8
R18.....	$C_4H + H_2 \rightarrow C_4H_2 + H$	$k_{18} = k_{17}$	5, 8
R19.....	$C_6H + H_2 \rightarrow C_6H_2 + H$	$k_{19} = k_{17}$	5, 8
R20.....	$C_2H + H + M \rightarrow C_2H_2 + M$	$k_{20} = \mathrm{Min}\ (1\times10^{-10}, 1.3\times10^{-23}\ T^{-2}\ M)$	11, 8
R21.....	$C_4H + H + M \rightarrow C_4H_2 + M$	$k_{21} = k_{20}$	11, 8
R22.....	$C_6H + H + M \rightarrow C_6H_2 + M$	$k_{22} = k_{20}$	11, 8
R23.....	$C_2H + C_4H_2 \rightarrow C_6H_2 + H$	$k_{23} = k_8$	5, 8
R24.....	$C_2H + C_6H_2 \rightarrow C_8H_2 + H$	$k_{24} = k_8$	5, 8
R25.....	$C_2H + C_8H_2 \rightarrow$ dust	$k_{25} = 1.0(-12)$	5, 8

[a] The complete set includes all the relevant reactions considered by Strobel 1973, 1974 and updated by Yung and Strobel 1980. Units for two-body rate coefficients are cm^3 $s/^1$. Globally averaged photodissociation rate constants at zero optical depth are given in s^{-1}. The numbers a $(-b)$ read as $a \times 10^{-b}$.

REFERENCES.—(1) Okabe 1978. (2) Van den Berg, Callear, and Norstrom 1969. (3) Parkes, Paul, and Quinn 1976. (4) Payne and Stief 1976. (5) Laufer and Bass 1979, with our estimate of the maximum possible activation energy. (6) Georgieff and Richard 1958. (7) Cross-sections shortward of 2000 Å from recent measurements by H. Okabe 1980 (private communication). (8) Estimated by the present authors. (9) Russell and Rowland 1979. (10) Pilling and Robertson 1975. (11) Yung and Strobel 1980, based on the reaction $CH_3 + H + M$.

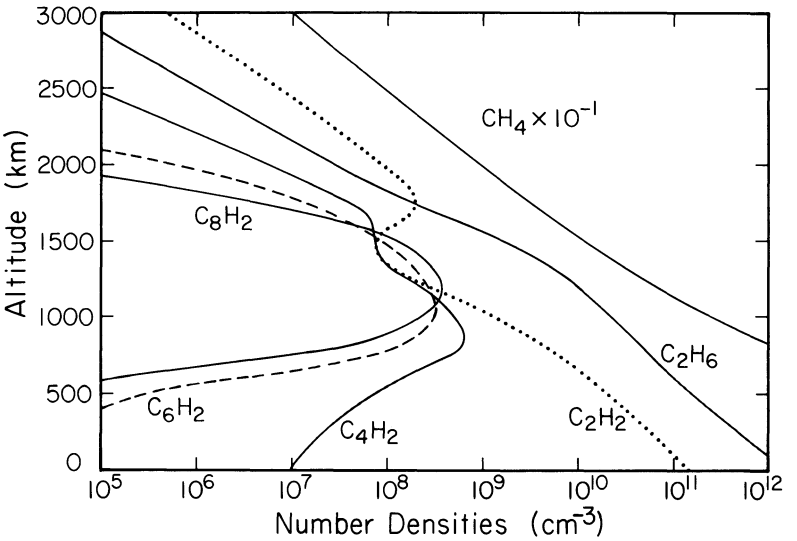

FIG. 2.—Number densities of the major hydrocarbons in the standard model. The column abundances for CH_4, C_2H_6, C_2H_4, C_2H_2, C_4H_2, C_6H_2, C_8H_2, H, and H_2 are, respectively, 8.2×10^{23}, 4.1×10^{19}, 5.3×10^{16}, 4.3×10^{18}, 3.2×10^{16}, 1.9×10^{16}, 1.9×10^{16}, 1.5×10^{18}, and 2.5×10^{22} cm^{-2}.

abstraction reactions R11, R12, and R13 (see Table 1), which contribute a total methane dissociation rate of 9.9×10^{10} cm^{-2} s^{-1}. By comparison, the direct photolysis rate is 1×10^{10} cm^{-2} s^{-1}.

To study the response of our atmosphere to the solar cycle, we made two steady state runs with $S = 5 \times 10^9$ and 2×10^{10} cm^{-2} s^{-1}. The column production rate of dust is very nearly proportional to S. The time constant for the system to respond to the Sun should be fast because of strong positive feedback reactions such as reactions R11 and R14 (Table 1). In an extended study, we intend to simulate the time-dependent photochemistry through the course of a solar cycle.

IV. CONCLUSION

Danielson dust is nearly ubiquitous in the upper atmospheres of the outer planets. The origin and chemical composition of this dust has remained a puzzle for nearly a decade, though a photochemical connection has long been suspected. The strength of our theory lies in its simplicity and in the number of definite predictions which can be tested immediately by suitable experimentation. In light of our theory, the early experiments of Scattergood and Owen (1977) should be repeated with C_2H_2 as a starting material rather than CH_4. There is indeed evidence in some work with polyacetylenes for the production of an intractable brown polymer (Tarr, Strausz, and Gunning 1965).

More extensive observations of C_2H_6, C_2H_4, and C_2H_2 on Titan are needed. It may be possible to detect the polyacetylenes directly by spectroscopic measurements in the ultraviolet and the infrared (Jones 1952; Lamotte, Binet, and Romanet 1977; Buijs and Ramsay 1980). The large variations in the photochemistry of the satellite over a solar cycle may be verified by long-term monitoring of the Lα cloud in the torus. Over geologic time, the total amount of accumulated photochemical products could amount to a crust as thick as 1 km, if uniformly spread over the satellite. The surface geology of Titan could be truly unique among all the objects in the solar system. The irreversible destruction of more than 100 atmospheres of methane should leave the atmosphere greatly enriched in the more inert gases such as N_2 and the noble gases.

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MARK ALLEN and YUK L. YUNG: Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125

JOSEPH P. PINTO: Goddard Institute for Space Studies, 2880 Broadway, New York, NY 10025